

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C03C 17/32, C09D 5/00	A1	(11) International Publication Number: WO 00/50354 (43) International Publication Date: 31 August 2000 (31.08.00)
(21) International Application Number: PCT/GB00/00534 (22) International Filing Date: 18 February 2000 (18.02.00) (30) Priority Data: 9904122.0 23 February 1999 (23.02.99) GB 9911344.1 14 May 1999 (14.05.99) GB (71) Applicant (for all designated States except US): BONAR POLYMERS LIMITED [GB/GB]; Horndale Avenue, Newton Aycliffe, County Durham DL5 6YE (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): MCDONALD, David, John [GB/GB]; 34 Pinewood Crescent, Heighington, County Durham DL5 6RP (GB). (74) Agent: STUTTARD, Garry, Philip; Urquhart-Dykes & Lord, Tower House, Merriion Way, Leeds LS2 8PA (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: GLASS COATING (57) Abstract A method for reducing the staining of glass sheets during transportation and storage by applying a coating of a polymer having acid groups.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

GLASS COATING

The present invention relates to the protection of glass and in particular to the protection of sheet glass. More particularly, the present invention relates to the protection of glass surfaces during storage and transportation.

It is known that glass surfaces are vulnerable to staining, in particular when the glass is newly made. Such staining manifests itself as iridescence. Staining is particularly noticeable when glass sheets are stacked side by side so that major surfaces are in adjacent face-to-face relationship. Staining occurs irrespective of whether the major faces are disposed horizontally or vertically or in an intermediate inclined position. The tendency to staining is particularly prevalent in hot humid conditions but is also a significant disadvantage in more temperate climates.

The present invention seeks to provide an improved method for protecting a glass surface by applying a stain-reducing amount of a polymeric solution to combat staining.

Thus viewed from one aspect the present invention provides a method for protecting a glass surface comprising:

forming a solution in a liquid carrier of a polymer having acid groups; and

applying the solution to the glass surface at an application rate of from about 40 to about 500mg of acid groups per square metre of glass surface whereby to form a water soluble coating to reduce iridescence.

Given that the method of the invention is particularly useful in guarding against staining during storage or transportation of a glass article (eg a sheet), it is

-2-

desirable that the solution is subsequently washed off with an aqueous solution (eg water) after storage or transportation.

Preferred acid groups are carboxyl (COOH) and sulphonic (HSO₃) groups. Related carboxyl groups such as acyl substituent groups may also be useful eg anhydrides.

Preferably the rate of application of the polymer is from about 50 to about 500 milligrams of acid groups per square metre of glass surface. In practice, the rate of application will be tailored to the climatic conditions (eg temperature and humidity) in which the glass surface is found. Generally speaking, in tropical conditions, application rates at the upper end of the range are preferred and in more temperate climates, the lower end is preferred.

Typically the rate of application may be measured by washing off the applied coating from a known area of glass (normally with distilled or demineralised water) and titrating against sodium or potassium hydroxide using an indicator (eg phenolphthalein indicator). By way of example, the following calculation may be used for polyacrylic acid:

Equivalent weight of polyacrylic acid = 72g
Equivalent weight of KOH = 56.11g (also = 1000ml of 1M KOH solution or 10000ml of 0.1M KOH solution)
1.0g of PAA = (10000/72) = 138.88ml of 0.1M KOH solution

Thus a solution containing 250mg of PAA will give a titre of 34.7mls of 0.1M KOH (or NaOH) or each mg of PAA will give rise to a titre of 0.1388ml of 0.1M KOH (or 1.388ml of 0.01M KOH). In order to equate this to a treatment level per square metre, the following expression is used:

-3-

Treatment level (in mg/m²) = titre/(area in m² x 0.1388)

Thus a litre of 7ml of 0.1M KOH from a sheet of 0.5m² area would indicate a treatment level of 100.8 mg/m² (and of course a titre of 70ml would be obtained from the same sheet using 0.01M KOH).

In a preferred embodiment the polymer has an acid value of 500mg/g or more, preferably 600mg/g or more. Preferably the acid value is in the range 500-1000mg/g, particularly preferably in the range 600-800mg/g. For example, polyacrylic acid has an acid value of about 760mg/g KOH and polymethacrylic acid has an acid value of about 652mg/g KOH.

The polymers for use in the invention may be homopolymers or heteropolymers. Preferred polymers are polymers of acrylic acid or methacrylic acid. For example, polyacrylic acid or polymethacrylic acid may be used. Sulphonic acid functional derivatives of polyolefins and polystyrene may also be suitable. Where the polymer is a heteropolymer, co-monomers may be selected from the group consisting of acrolein, simple or branched alkyl (eg C₁₋₆-alkyl) or hydroxyesters of acrylic acid or methacrylic acid, vinyl derivatives of benzene or toluene (eg styryl or cinnamyl), vinyl esters of organic acids (eg vinylC₁₋₆-carboxylates such as vinyl acetate, vinyl butyrate and vinyl propionate) and maleic anhydride.

The polymer may have a molecular weight between preferred upper and lower limits. The choice of these limits will be within the capabilities of the man skilled in the art. Nevertheless, below a molecular weight of about a few hundred there may be little or no film-forming effect. The upper limit of the molecular weight may be as high as several million. However, above a molecular weight of about 600,000,

-4-

the polymer chains may be sufficiently sterically hindered in solution so as to lose their effective carboxyl or other concentration. In the downstream handling of the "glass stack" of which the glass surface is a part, it is desirable that the applied solution is capable of being washed off. This has an effect on the choice of the upper limit of the molecular weight range because as the molecular weight increases the ease of solubilisation decreases. Generally speaking, a preferred molecular weight range is 10,000 to 600,000.

The preferred polymers for use in the method of the invention are polymers of acrylic acid or methacrylic acid (eg polyacrylic acid or polymethacrylic acid) having molecular weights in the range of about 10,000 to about 600,000 and solution viscosities (in water or organic solvent) of about 12 to about 100 centipoises, at 5% polymer concentration and 25°C.

The solution may be applied to the glass surface in any suitable manner. Surfactants may be present to assist wetting of the glass surface. De-foamers or anti-foamers may also be present to suppress the tendency to foam which may otherwise hinder the formation of a coating of the polymer on the glass surface. In addition, dyes may be present. Other optional ingredients may be used provided that they do not reduce the effect of the acid groups in the applied composition.

Typically, the glass surface will be part of a sheet (eg a flat glass or float glass sheet).

Viewed from a further aspect the present invention provides a glass sheet having on at least one surface thereof a coating of a polymer solution having acid groups in sufficient concentration to reduce iridescence. Preferably

-5-

the extent of coverage is 40 to about 500 milligrams of acid groups per square metre of glass surface. Preferably, the glass sheet is obtainable by a method as hereinbefore defined.

The present invention will now be described in a non-limitative sense with reference to the following examples:

Example 1

A formulation comprising:

100g of an aqueous solution of polyacrylic acid (Acrysol A1/Primal A1/Acumer 1510 - Rohm & Haas) at a concentration of 25wt% and a molecular weight of approximately 20,000,
1.0g of silicone oil emulsion (NL65 - Dow Corning),
0.3g non-ionic surfactant (Nonidet LE - Shell) and
0.1g cochineal dye (Carmoisine - Supercook),
2400g water

was sprayed onto a glass sheet to form a continuous functional film which was ultimately easily removable with water. The film reduced the risk of iridescent staining.

Example 2

A formulation comprising:

160g of an aqueous solution of polyacrylic acid (Glascol E7 - Ciba Speciality Chemicals) at a concentration of 25wt% and a molecular weight of approximately 30,000,
1.5g of hydrophobic silica in mineral oils (Contrapen PR/388 - Lamirsa Laboratories Miret SA),
0.3g non-ionic surfactant (Nonidet LE - Shell) and
0.1g cochineal dye (Carmoisine - Supercook),

1350g water

was sprayed onto a glass sheet to form a continuous functional film which was ultimately easily removable with water. The film reduced the risk of iridescent staining.

Example 3

A formulation comprising:

160g of an aqueous solution of polyacrylic acid (Glascol E9 - Ciba Speciality Chemicals) at a concentration of 25wt% and a molecular weight of approximately 75,000,
1.5g of hydrophobic silica in mineral oils (Contrapen PR/388 - Lamirsa Laboratories Miret SA),
0.3g non-ionic surfactant (Nonidet LE - Shell) and
0.1g cochineal dye (Carmoisine - Supercook),
1350g water

was sprayed onto a glass sheet to form a continuous functional film which was ultimately easily removable with water. The film reduced the risk of iridescent staining.

Example 4

A formulation comprising:

160g of an aqueous solution of polyacrylic acid (Glascol E11 - Ciba Speciality Chemicals) at a concentration of 25wt% and a molecular weight of approximately 250,000,
1.5g of hydrophobic silica in mineral oils (Contrapen PR/388 - Lamirsa Laboratories Miret SA),
0.3g non-ionic surfactant (Nonidet LE - Shell) and
0.1g cochineal dye (Carmoisine - Supercook),
1350g water

was sprayed onto a glass sheet to form a continuous functional film which was ultimately easily removable with water. The film reduced the risk of iridescent staining.

Example 5

A formulation comprising:

160g of an aqueous solution of polyacrylic acid (Glascol K11 - Ciba Speciality Chemicals) at a concentration of 25wt% and a molecular weight of approximately 10,000,
1.5g of hydrophobic silica in mineral oils (Rhodoline DF6681 - Rhodia),
0.3g non-ionic surfactant (Nonidet LE - Shell) and
0.1g cochineal dye (Carmoisine - Supercook),
1350g water

was sprayed onto a glass sheet to form a continuous functional film which was ultimately easily removable with water. The film reduced the risk of iridescent staining.

CLAIMS:

1. A method of protecting a glass surface comprising:
forming a solution in a liquid carrier of a polymer having acid groups; and
applying the solution to the glass surface at an application rate of from about 40 to about 500mg of acid groups per square metre of glass surface whereby to form a water soluble coating to reduce iridescence.
2. A method as claimed in claim 1 comprising the step of:
washing the applied solution off the glass surface with an aqueous solution at the end of the desired period.
3. A method as claimed in either of claims 1 or 2 wherein the polymer is a polymer or co-polymer comprising a monomer selected from the group consisting of acrolein, vinyl derivatives of benzene or toluene, vinyl derivatives of organic acids, simple or branched alkyl or hydroxyesters of acrylic acid or methacrylic acid and maleic anhydride.
4. A method as claimed in either of claims 1 or 2 wherein the polymer is a polymer of acrylic acid, methacrylic acid or a sulphonic acid functional derivative of a polyolefin or polystyrene.
5. A method according to claim 4 wherein the polymer is a polymer of acrylic acid or methacrylic acid having a molecular weight in the range of about 10,000 to about 600,000.
6. A method as claimed in claim 5 wherein the polymer is applied in solution having a solution viscosity

(in water or in organic solvent) of about 12 to about 100 centipoises at 5% polymer concentration and 25°C.

7. A method as claimed in any preceding claim wherein the polymer has an acid value of 500mg/g or more.

8. A method as claimed in claim 7 wherein the polymer has an acid value of 600mg/g or more.

9. A method as claimed in claim 7 or 8 wherein the polymer has an acid value in the range 500-1000mg/g.

10. A method as claimed in claim 7, 8 or 9 wherein the polymer has an acid value in the range 600-800mg/g.

11. A glass sheet having on at least one surface thereof a coating of a polymer having acid groups in sufficient concentration to reduce iridescence.

12. A glass sheet as claimed in claim 11 having an extent of coverage being about 40 to about 500mg of acid groups per square metre of glass surface.

13. A glass sheet as claimed in claim 11 obtainable by a method as defined in any of claims 1 to 10.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/00534

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C03C17/32 C09D5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C03C C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 543 514 A (PPG INDUSTRIES INC.) 5 October 1984 (1984-10-05) claims	1-13
Y	US 4 055 441 A (L. JOHNSTON TAYLOR ET AL.) 25 October 1977 (1977-10-25) column 3, line 26 - column 4, line 52	1-13
X	US 4 053 666 A (TAYLOR LYNN J ET AL) 11 October 1977 (1977-10-11) abstract	1,3-13
X	GB 1 125 142 A (S.C. JOHNSON) 28 August 1968 (1968-08-28) page 32, line 74 - line 87	1,3-13
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

25 May 2000

Date of mailing of the international search report

02/06/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Reedijk, A

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 00/00534

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 99 24255 A (C. PAGANO ET AL.) 20 May 1999 (1999-05-20) page 4, line 20 -page 5, line 27 ----	1-4
A	US 4 489 106 A (P.F. DUFFER ET AL.) 18 December 1984 (1984-12-18) claims ----	1-13
A	DATABASE WPI Section Ch, Week 199030 Derwent Publications Ltd., London, GB; Class A14, AN 1990-224956 XP002122794 & DD 276 084 A (FR-SCHILLER-UNIV JENA), 14 February 1990 (1990-02-14) abstract ----	1-13
A	GB 2 145 640 A (U C B S A) 3 April 1985 (1985-04-03) examples ----	1-13
A	US 3 577 256 A (C.L. BENFORD ET AL.) 4 May 1971 (1971-05-04) column 2, line 6 - line 43 ----	1-13
A	US 4 517 242 A (SINHA KAMAL R ET AL) 14 May 1985 (1985-05-14) -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/00534

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
FR 2543514	A	05-10-1984	CA	1243568 A	25-10-1988
			IT	1173538 B	24-06-1987
			US	5026597 A	25-06-1991
			CA	1258998 A	05-09-1989
US 4055441	A	25-10-1977	US	4053666 A	11-10-1977
US 4053666	A	11-10-1977	US	4055441 A	25-10-1977
GB 1125142	A		AU	410709 B	22-02-1971
			AU	6345265 A	02-03-1967
			DE	1519201 A	05-03-1970
			FR	1549166 A	13-12-1968
			SE	317758 B	24-11-1969
			US	3308078 A	07-03-1967
WO 9924255	A	20-05-1999	US	5962565 A	05-10-1999
US 4489106	A	18-12-1984	CA	1213509 A	04-11-1986
			FR	2533552 A	30-03-1984
			IT	1171704 B	10-06-1987
DD 276084	A	14-02-1990	NONE		
GB 2145640	A	03-04-1985	BE	897931 A	06-04-1984
US 3577256	A	04-05-1971	NONE		
US 4517242	A	14-05-1985	US	4517243 A	14-05-1985